

## SELF-DIFFUSION OF CATIONIC CHROME COMPLEXES THROUGH CATIONIC EXCHANGERS

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### ABSTRACT

The self-diffusion of the cationic complexes present in chromium sulfate solution through carboxylic and sulfonic type cation exchange resins was studied by addition of isotopic sulfur and chromium in the solution and kinetically following their exchange in the resin phase already equilibrated. Diffusion through the particle of the resin was observed to be the rate-determining step under the conditions used. The values of the exchange rate constants and the diffusion coefficients and their dependence on the concentration of chromium, size of resin and temperature were evaluated. Results lead to the conclusion that carboxyl resins differ from sulfonic resins in that carboxyl resins cause displacement of sulfate from the chromium complex.



### INTRODUCTION

In tanning processes, the fundamental rate step is not yet well understood. Kinetic studies on chrome tanning were reported by Briggs (1). It is known that relatively slow rates were due to diffusion of solutes through the fiber structure of the hide or skin (2). Molecules above a critical size are incapable of penetrating the fibers because of steric factors. Scanty information is available on determination of the size of the chrome complex (3). In order to understand the process occurring within the collagenous net-work as penetration proceeds, a complete knowledge of the diffusion properties of the solute within the absorbent is required. This is difficult to obtain for the system under consideration viz., hide or skin, since not only the rate constant representing the diffusion flow but also the dimensions, inter-molecular forces and electrochemical nature of the three dimensional, helical structure constituting the solid phase, change continuously during the process. Hence it is proposed to present initially a brief account of diffusion in general terms from the data obtained with a more simple

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system like the monofunctional organic exchangers which can be, to some extent, considered as model substances of natural ion exchange materials like proteins, wool, cell membranes, etc. Except for one paper on diffusion studies in leather using isotopes (4), there is no citation in the literature using isotopes for a similar study.

This paper deals with the kinetics of self-diffusion of the cationic chromium complexes present in a 33 percent basic chromium sulfate liquor, which is the most important from the point of view of chrome tanning. A direct approach to the measurement of the diffusion coefficient in any system involved the measurement of the distribution of solute at various times, so that concentrations at various distances from the interphase boundary may be ascertained. The tracer technique makes the system simpler, because the diffusion of only the radioactive isotopes is involved, and the analytical work is greatly simplified. In all cases the concentration at the surface is maintained constant by using a large excess of solute in the external solution. When the volume of the system remains constant, the mathematical treatment is relatively simple in terms of the second law of Fick (5). Generally, in ion exchange reactions, the rate of exchange is controlled by one or both of the following processes: (a) diffusion through the polymeric structure of the exchanger ("particle diffusion"); (b) transportation of ions through a "Nernst film," created by a concentration gradient, surrounding the particles ("film diffusion") (6). The first process prevails in concentrated, the second in dilute, solutions. In the present work the formation of the film was prevented by thorough agitation of the external solution.

Since the chrome liquor contains more than one type of complex, only apparent self-diffusion coefficients are reported. Measurements were made at various temperatures, different concentrations of solute in the external solution, and different sizes of the resin. In most of the experiments both the  $^{51}\text{Cr}$  and  $^{52}\text{S}$  were followed by tracer technique.

#### EXPERIMENTAL

(a) **Chrome liquor:** The 33 percent basic chromium sulfate was prepared by reducing a mixture of equimolar quantities of chromic acid and sulfuric acid gradually by means of hydrogen peroxide. The resulting solution was diluted to contain one mole of chromium per liter and aged for several weeks to attain equilibrium. The pH of the solution was about 3.0 and it contained about 90 percent cationic chromium complexes.

(b) **Ion exchange resin:** The resins used were Amberlite IRC-50 (Carboxyl type) or Amberlite IR-120 (sulfonic type) (analytical grades) of 20-60 mesh size. The resin Amberlite IRC-50 was partly converted ( $\sim 30$  percent) to the sodium form by repeated equilibrium with 2 N NaOH-1 percent NaCl mixture to attain an equilibrium pH 4.0 (optimum value where hydrolysis of chromium sulfate will not lead to precipitation of chromium hydroxide) and

washed with cold water of the same pH until the effluent was free of chloride ions. The capacity of the resin was determined by the usual titration method (7) and found to be 6.31 meq.  $H^+$ /g. of air dried resin. The Amberlite IR-120 resin was adjusted to pH 4.0 with NaOH. The resins were sieved through appropriate meshes repeatedly and beads of definite sizes were chosen for the experiment.

(c) **Isotopes:**  $^{51}Cr$  as  $CrCl_3$  in HCl solution and  $^{32}S$  as  $H_2SO_4$  in dilute HCl solution (carrier free) were supplied by the Bhabha Atomic Research Centre, Trombay, Bombay.

(d) **Kinetic measurements:** Modified limited bath technique (6b) was used. Preliminary studies were conducted including sorption and desorption studies to ensure proper experimental conditions for a particle diffusion controlled process. Chrome liquor diluted to the required concentration (250 ml.) was taken in a 500 ml. round bottomed flask. The concentration of the cations was kept sufficiently in excess of the resin capacity. Ten grams of the appropriate ion exchanger was suspended in it and the flask was submerged in a thermostatic bath held to  $\pm 0.2^\circ C.$  of the desired temperature. The contents of the flask were kept thoroughly stirred by means of a magnetic stirrer. Three to four days were allowed to ensure complete thermal equilibration and uptake of the cationic complexes by the resin. The self exchange reaction was initiated by adding definite quantities of the  $^{51}Cr$  and  $^{32}S$  isotope to the external solution and following their uptake in the resin by removing small quantities of resin at definite time intervals and analyzing it for the  $^{51}Cr$  and  $^{32}S$  activity. Runs were followed till the isotopic equilibrium was attained.

(e) **Radioactive assays:**  $^{51}Cr$  : The ion exchange resin was washed several times with cold water and filtered through a preweighed aluminum planchet. It was dried, weighed and covered with cello tape. The activity ( $t_{1/2} = 27.8$  days;  $E_{max}$  for  $\gamma = 0.323$  MeV) of the sample was measured with a head type scintillation unit coupled with a discriminator. The scintillator is a sodium iodide (thallium activated) crystal optically coupled to the photomultiplier cathode.  $^{32}S$  : The ion exchange resin after washing was dried. A known quantity was suspended in water and then heated with sodium peroxide. A known amount of sodium sulfate was added as a carrier. After adjusting the pH to 2-3 and reduction of  $Cr^{6+}$  to  $Cr^{3+}$  by the hydrogen peroxide present, the sulfate was precipitated as benzidine sulfate. The precipitate was centrifuged, washed with water, acetone and ether, dried and the specific activity ( $t_{1/2} = 87.2$  days;  $E_{max}$  for  $\beta = 0.167$  MeV) was determined by counting at the same position to ensure identical geometry, under a GM end window type counter having a window thickness of 2-3 mg./cm<sup>2</sup>. Self-absorption correction was eliminated, since measurements of activity were done in the infinitely thick region.

Statistical error was kept at a minimum (0.5 percent) by taking sufficiently large counts in the scaler for each measurement. Corrections were applied for

dead time loss, self-decay and background. From the specific activity, the fraction exchange (F) values were obtained using the relationship  $1 - F = \frac{S_t - S_\infty}{S_0 - S_\infty}$

where  $S_0$ ,  $S_t$  and  $S_\infty$  represent specific activity values initially, at time 't' and after the attainment of equilibrium (8).

## RESULTS AND DISCUSSION

As the limited bath method was used for the kinetic measurements, the equations developed by Boyd *et al.* (6a) and by Kressman *et al.* (6b) hold good. If diffusion within the resin is the slow step (particle diffusion) the rate should follow the equation

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \text{ where } B = D\pi^2/r^2 \dots\dots\dots(1)$$

This equation has been derived formulating the differential equation for the distribution of the solute between the solid and solution phase, solving the same for boundary conditions as applicable and summing up for the total amount of solute entering per unit area in a given time. The fraction of the solute adsorbed at any time to the amount adsorbed at equilibrium gave the expression for F as an exponential function of diffusion coefficient, temperature and inverse of the square of resin diameter.

or

$$F = \frac{6}{r} \frac{Q_0}{Q_0 - Q_\infty} \sqrt{\frac{Dt}{\pi}} \dots\dots\dots(2)$$

where F is the fraction exchanged and is given by  $Q_t/Q_\infty$ .  $Q_t$  is the amount of exchange in time t,  $Q_\infty$  is that at infinite time and  $Q_0$  is the total amount of resin and solute used in the kinetic run; 'r' is the radius of the spherical particles in cms. and D is the diffusion coefficient in sq.cm./sec. inside the resin. The magnitude of B is also a measure of the exchange rate constant for the diffusion process with second<sup>-1</sup> as dimension (9). When B and 'r' remain constant in a particular experiment, as in the case of isotope exchange, linear plots are obtained for Bt vs t (Eq. 1) or F vs  $\sqrt{t}$  (Eq. 2). If film diffusion or chemical reaction is the rate determining step then a plot of  $\log(1 - F)$  vs t will be a straight line (6a), since in such cases mass action rate equation alone holds good where  $\log(1 - F)$  is directly proportional to 't'.

Preliminary studies on sorption and desorption of chrome complexes in chrome liquor by ion exchangers indicated the particle diffusion mechanism. Plots of Bt vs t and F vs  $\sqrt{t}$  gave straight lines like those in Figures 1 and 2 and, from the slope, the diffusion coefficient values were evaluated. The value for desorption of chrome complexes ( $D_d$ ) with carboxyl exchanger was  $1.018 \times 10^{-10}$  cm.<sup>2</sup>/sec and for sorption ( $D_s$ )  $1.514 \times 10^{-10}$  cm.<sup>2</sup>/sec respectively. The sorption process was observed to be a rapid one, as is evident from the diffusion coefficient

value and also from the short time for half exchange (3-4 hours). If  $D$  is constant then  $D_s = D_a$  and the absorption and desorption curves are identical. When  $D$  increases with  $C$  then  $D_s > D_a$  and the integral diffusion coefficient  $\bar{D}$  is given by (10)  $\bar{D} \sim \frac{1}{2} (D_s + D_a)$ .

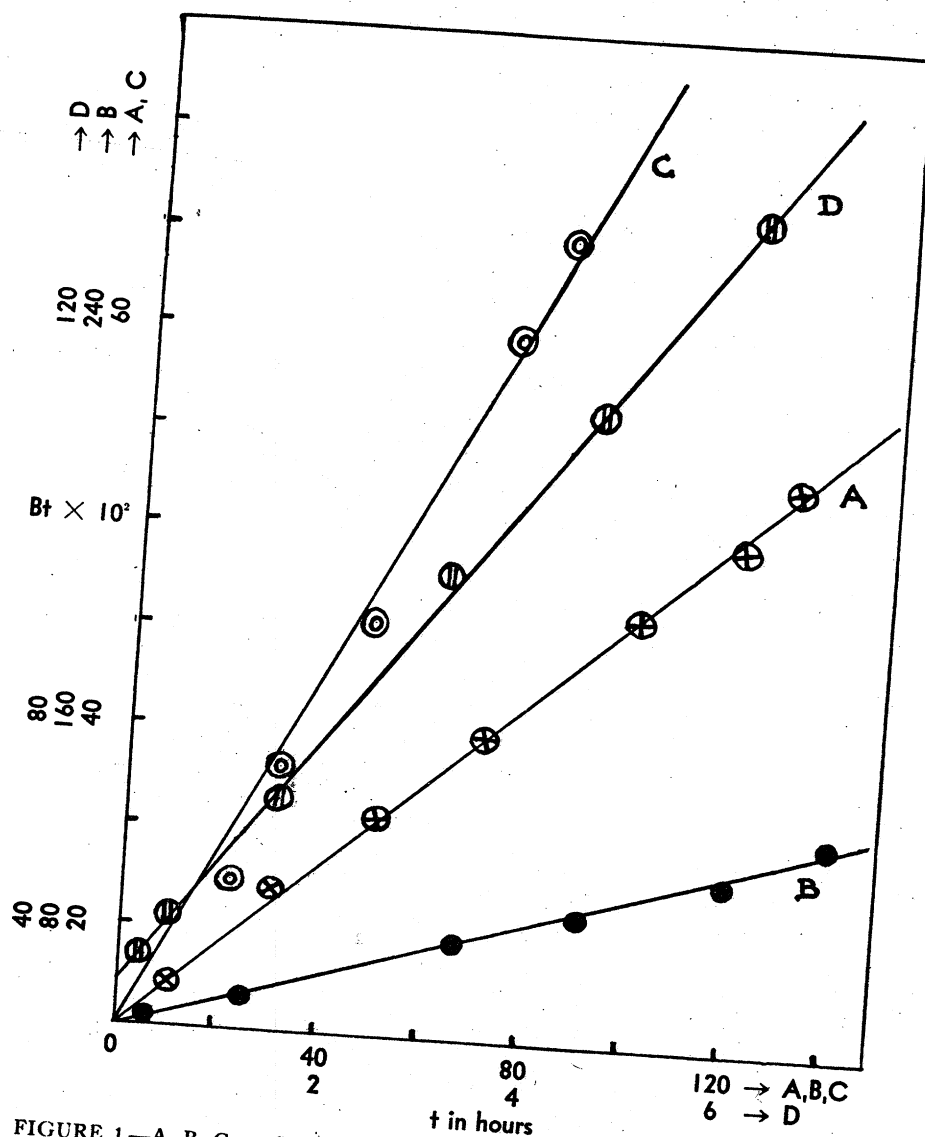


FIGURE 1.—A, B, C — Amberlite IRC-50;  $[Cr] = 0.2111$  M;  $r = 0.0302$  cm;  
A = 30°C.; B = 35°C.; C = 40°C.  
D — Amberlite IR-120;  $[Cr] = 0.2111$  M.  
 $r = 0.0302$  cm; Temp. = 30°C.

Self diffusion experiments with Amberlite IRC-50 showed that diffusion through the resin particle was rate controlling. This is clearly seen from the linearity of the plots of  $Bt$  vs  $t$  and  $F$  vs  $\sqrt{t}$  as shown in Figures 1 and 2. Values of  $Bt$  for each value of  $F$  were taken from the computed values given by Reichen-

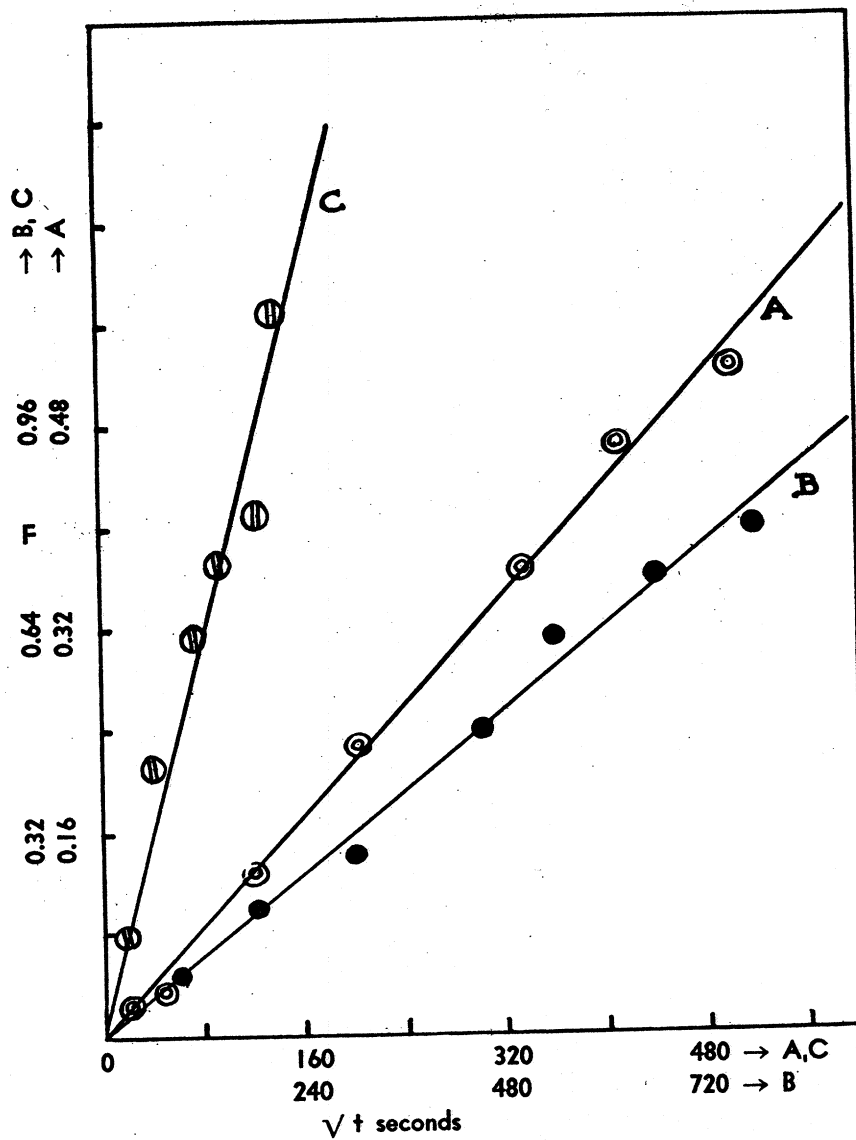


FIGURE 2.—A — Amberlite IRC-50;  $[Cr] = 0.0897$  M;  $r = 0.023$  cm; Temp. =  $30^{\circ}\text{C}$ .  
 B — Amberlite IRC-50;  $[Cr] = 0.0996$  M;  $r = 0.0302$  cm; Temp. =  $30^{\circ}\text{C}$ .  
 C — Amberlite IR-120;  $[Cr] = 0.2111$  M;  $r = 0.0302$  cm; Temp. =  $30^{\circ}\text{C}$ .

berg (9). That neither a chemical reaction nor a film diffusion process was rate controlling is evident from a plot of  $-\log(1 - F)$  vs  $t$  as shown in Figure 3. From the slopes of the curves in Figures 1 and 2 the diffusion coefficient was evaluated knowing the value of ' $r$ '. The values from the two different plots were in good agreement. The slope from Figure 1 gave directly the rate constant for

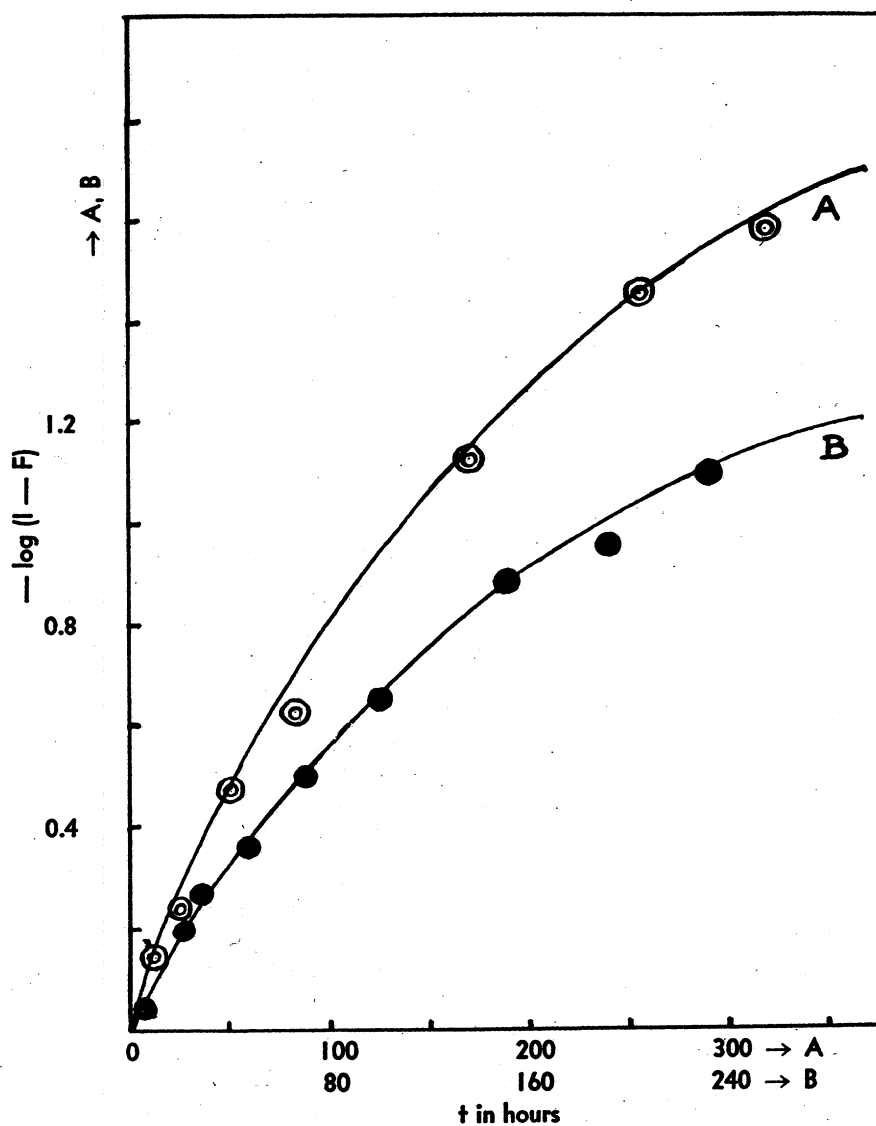


FIGURE 3.—A — Amberlite IRC-50;  $[Cr] = 0.2000$  M;  $r = 0.023$  cm; Temp. =  $30^{\circ}\text{C}$ .  
B — Amberlite IRC-50;  $[Cr] = 0.2111$  M;  $r = 0.0302$  cm; Temp. =  $40^{\circ}\text{C}$ .

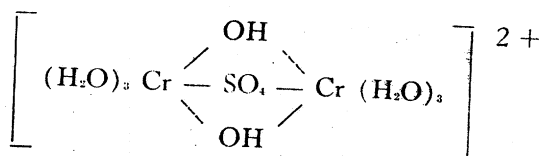
the diffusion process. That particle diffusion mechanism is the controlling factor is further substantiated by the constancy in the values of the diffusion coefficients within the limit of experimental error when the concentrations of the external solution were changed. Table I shows the rate constant and the diffusion coefficient values at different concentrations of chromium.

TABLE I  
EFFECT OF CONCENTRATION OF CHROMIUM ON THE DIFFUSION  
COEFFICIENT AND RATE CONSTANT WITH IRC-50 RESIN

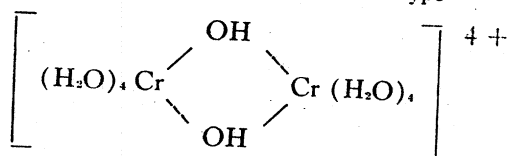
Chromium Concentration Moles/lit.	Rate Constant 'B' sec <sup>-1</sup> × 10 <sup>6</sup>	Diffusion Coefficient 'D' cm <sup>2</sup> /sec.
0.0897	1.683	9.014 × 10 <sup>-11</sup>
0.0996	1.926	9.643 × 10 <sup>-11</sup>
0.2000	1.970	1.055 × 10 <sup>-10</sup>
0.4511	2.130	1.012 × 10 <sup>-10</sup>

(Temp. 30°C.; 'r' = 0.023 cm.; Resin IRC-50 Carboxylic Type)

33 percent basic chrome liquor has been reported to contain complexes of the type (11).



together with a certain percentage of complexes of the type



In all the experiments, both the <sup>51</sup>Cr and <sup>35</sup>S activity were followed in the resin phase. It was found that, with the carboxylic resin, exchange of <sup>35</sup>S was practically negligible, except for a small uptake, although considerable exchange of Cr occurred. It was also found that a major fraction of <sup>35</sup>S was present in the complex form in the solution phase. The absence of isotopic exchange of sulfur with the resin phase, after a slight initial uptake, apparently indicates the absence of coordinated sulfate in the chrome complex of the resin phase. Since there was a regular increase in the activity of chromium in the resin, this might suggest that the resin had preferentially taken up sulfate-free complexes; but the presence of a constant amount of activity due to sulfur in the resin phase is against this preferential uptake. The reason for this peculiar phenomenon will



TABLE II  
KINETICS OF EXCHANGE OF ISOTOPIC CHROMIUM AND SULFUR  
IN CARBOXYLIC AND SULFONIC TYPE RESINS

AMBERLITE IRC-50 (Carboxylic)			AMBERLITE IR-120 (Sulfonic)		
Time in Hrs.	Sp. Activity for Chromium	Sp. Activity for Sulfur	Time in Hrs.	Sp. Activity for Chromium	Sp. Activity for Sulfur
—	1.192	326	—	12.55	5
6	1.369	867	0.5	34.25	228
23	3.387	828	1.5	44.44	341
30.25	4.547	843	3.0	54.13	478
97.75	9.913	902	4.5	56.84	564
195.25	14.624	875	6.0	59.62	640
412	20.734	981	22.5	63.23	764

(Temp. 30°C.; [Cr] = 0.2111 M; 'r' = 0.023 cm.)

Theoretically the tetrapositive complex is likely to be smaller in dimension compared to the sulfato bipositive complex. The ion exchange resin will take complexes of higher charges preferentially and also those of smaller dimensions (7), since the size of the complex is a major criterion in the particle diffusion mechanism. If this is so, the constancy in the sulfur activity is understandable for the carboxylic resin, since the concentration of chromium in the solution taken is in large excess. However, the same explanation cannot hold for the increase in sulfur activity for the sulfonic resin.

The tracer diffusion coefficient values in the experiments were of the order of  $10^{-10}$  cm<sup>2</sup>/sec for the carboxyl type resins at 30°C. Diffusion coefficients in sulfonic type resins for bipositive and tetrapositive metal ions at 25°C. were reported to be of the order  $10^{-8}$  and  $10^{-10}$  cm<sup>2</sup>/sec respectively (18). A comparatively low value for the tracer diffusion in the present case is probably due to the steric hindrance offered by the polynuclear complexes.

The influence of the size of the resin plays an important role in a particle diffusion controlled process. The influence will be manifested in the B value, the D value remaining constant as indicated in Table III.

TABLE III  
EFFECT OF PARTICLE SIZE ON THE DIFFUSION COEFFICIENT  
OF CHROMIUM SPECIES WITH CARBOXYLIC EXCHANGER

Particle Radius in cm.	Rate Constant B sec. <sup>-1</sup> × 10 <sup>6</sup>	Diffusion Coefficient D cm <sup>2</sup> /sec. × 10 <sup>10</sup>
0.023	1.968	1.051
0.0302	1.176	1.087

(Temp. 30°C.; [Cr] = 0.2111 M; Amberlite IRC-50)

The temperature dependence of the diffusion reaction was studied and both the rate of diffusion and the diffusion coefficients were affected, as shown in Table IV. This trend is in conformity with a particle diffusion controlled process.

TABLE IV  
EFFECT OF TEMPERATURE ON THE DIFFUSION COEFFICIENT  
OF CHROMIUM SPECIES WITH CARBOXYLIC EXCHANGER

Temp. °C.	Rate Constant B sec. <sup>-1</sup> × 10 <sup>6</sup>	Diffusion Coefficient D cm <sup>2</sup> /sec. × 10 <sup>10</sup>
30	1.176	1.087
35	1.666	1.539
40	2.605	2.405

([Cr] = 0.2111 M; 'r' = 0.0302 cm.; Amberlite IRC-50)

The energy of activation has been evaluated by making use of the equation

$$\ln D_1 - D_2 = - \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

The linear variation of log<sub>10</sub> D with 1/T also indicated that Arrhenius equation  $D = D_0 \exp(-E/RT)$  is valid (19). The calculated activation energy value 18.06 Kcal/mole is much higher than the value 5–10 Kcal/mole reported (6b, 9) for the exchange of monovalent cations in strong cation exchangers in the H<sup>+</sup> form. In their studies on the exchange of bipoisitive cations on the chelating resin Bio-chelex 100 in the H<sup>+</sup> form Wirguin *et al.* (20) have observed a high value of 12–17 Kcal/mole and they attribute it to the probable low swelling of the resin. The high value in the present system may also be due to the complex nature of the diffusing species making the effective path length greater.

#### CONCLUSIONS

Isotopic exchange of chrome complexes is controlled by particle diffusion. Carboxylic and sulfonic type cation exchangers exhibit significant differences in their behavior. Sorption of complexes by carboxyl resins is very rapid compared to that of the sulfonic type. Also carboxyl resins cause displacement of sulfate from the adsorbed chromium complex.

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